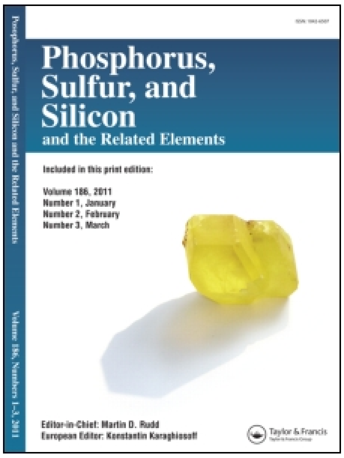

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Banert, Klaus , Fendel, Wolfgang , Müller, Anett , Müller, Beate and Schlott, Jana(1999) 'Synthesis of New 1,3-Butadienes with Sulfur-Containing Functional Groups by Sigmatropic Rearrangements', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 325 — 326

To link to this Article: DOI: 10.1080/10426509908546453

URL: http://dx.doi.org/10.1080/10426509908546453

Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 325-326
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Synthesis of New 1,3-Butadienes with Sulfur-Containing Functional Groups by Sigmatropic Rearrangements[1]

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A variety of novel 1,3-butadienes with one or two sulfur-containing groups are easily accessible by sigmatropic rearrangement reactions. Furthermore, a new sequence of sigmatropic migrations leads to 1,2-difunctionalized 1,3-butadienes.

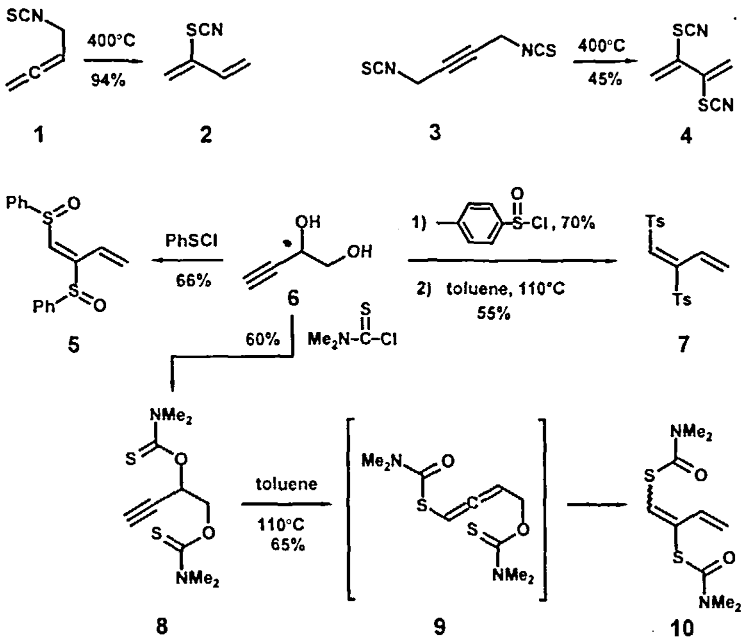
Keywords: sigmatropic rearrangements; functionalized 1,3-butadienes

INTRODUCTION

Several 1,3-butadienes with sulfur-containing functional groups can be prepared by [3,3] or [2,3] sigmatropic rearrangement reactions via allenes[2].

SYNTHESIS OF NEW MONOFUNCTIONALIZED AND DIFUNCTIONALIZED 1,3-BUTADIENES

Starting with 2,3-butadienyl or 2-butyne-1,4-diyl precursors like **1** or **3**, new 1,3-butadienes with one or two sulfur-containing functional groups can be prepared (Scheme). In the case of the products **2** and **4**, the [3,3] sigmatropic rearrangement reactions, which are performed on flash vacuum pyrolysis, transform the isothiocyanato groups into the thermodynamically less stable thiocyanato functions. Obviously, conjugation of C,C double bonds and the thiocyanato groups overcompensates this disadvantage.[3]



SYNTHESIS OF 1,2-DIFUNCTIONALIZED 1,3-BUTADIENES BY A NOVEL SEQUENCE OF SIGMATROPIC MIGRATIONS

The alcohol **6** is the ideal starting material to prepare precursors for a new sequence of sigmatropic rearrangements, which produces 1,2-difunctionalized 1,3-butadienes like **5**, **7**, and **10**.[4] Two consecutive migrations, for instance **8** → **9** → **10**, direct both functional groups into vinylic positions (Scheme).

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